

High Throughput Mineral Oil Analysis (Hydrocarbon Oil Index) by GC-FID Using the Agilent Low Thermal Mass (LTM) System

Application Note

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Abstract

Cycle time for gas chromatography-flame ionization detection analysis of mineral oil in environmental samples was dramatically reduced and the sensitivity increased by fast oven temperature programming using a low thermal mass system. Regulated method requirements are met for the environmental analysis of the C₁₀-C₄₀ hydrocarbon fraction in soil and water extracts using splitless injection with an analysis time less than three minutes. Cool-down time is less than two minutes, resulting in an injection-injection cycle time of five minutes. Method performance criteria, including repeatability, linearity and solute discrimination are presented.



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Introduction

Environmental contamination by hydrocarbon fractions, such as diesel or motor oil, is currently measured using gas chromatography with flame ionization detection (GC-FID). This method, also called hydrocarbon oil index (HOI), mineral oil, or total petroleum hydrocarbon (TPH) determination is one of the most important applications in environmental analysis because it represents the highest sample loads in many laboratories. For analysis, samples (water, soil, sediment) are extracted by an apolar (hydrocarbon) solvent with a boiling point between 36 °C and 69 °C (for example, hexane). The extract is cleaned by passing over Florisil (to retain more polar solutes such as lipids), concentrated by N₂ blow down (or Kuderna-Danish) and analyzing by GC-FID [1]. The fraction eluting on an apolar (HP-1, HP-5) column between decane (C₁₀) and tetracosane (C₄₀) is defined as “mineral oil” or “HOI”, over which the area is summed for quantitation.

The ISO 9377 method specifies the use of a column with a high phase ratio (thin film) to facilitate elution of C₄₀. GC oven program conditions should also allow the separation of the extraction solvent from the first peak (decane). Therefore, low initial temperatures (35 °C to 40 °C) are often necessary. Minimal solute discrimination is an important requirement of the injection method. The method specifies that the relative mass response for tetracosane and eicosane (C₂₀) should be higher than 0.80. Typically, the analysis is performed using a 10 to 30-m column using splitless, programmable temperature vaporizing (PTV) or cool on-column injection and oven programming from 40 °C to 340 °C at 10 to 20 °C/min, resulting in analyses times of 20 to 30 min [2]. Oven cool-down time to the low initial temperature typically requires an additional 5 min or more, resulting in a total cycle time of 30 min or longer.

Currently, environmental laboratories are seeking ways to improve throughput and decrease cost per sample. Significantly improved cycle times can be achieved by adding an LTM module to an Agilent 7890A GC system with a split/splitless inlet (SSI), fast automatic liquid sampler (7683B or 7693A), and FID. In this application note, optimized method conditions and performance metrics are presented. Cycle times of 5 min are demonstrated, while still meeting all method requirements.

Experimental Conditions

Solute and Sample Preparation

An alkane standard containing even numbered n-alkanes from C₁₀ to C₄₀ was purchased from Restek (cat. no 31678, Restek, Bellefonte, USA). The sample was diluted to 5 ng/μL in hexane. Mineral oil calibration was done using a 1:1 mixture of diesel and motor oil (cat. no 31630, Restek). Calibration samples were prepared at concentrations between 40 and 1000 mg/L in hexane. In addition, a reference sample from RIVM (NMI, The Netherlands) containing diesel and motor oil was used. This sample was diluted at 1000 mg/L in hexane.

GC-FID Conditions

Analyses were performed on an Agilent 7890A GC System equipped with an SSI, FID and an LTM column module containing a 10 m × 0.32 mm, 0.1 μm DB-5HT column (to order, use p/n 100-2000LTM for custom LTM column, and state 123-5701 with “long legs” in the description) connected directly to an SSI and FID.

The fast GC conditions are listed in Table 1.

Table 1. GC-FID Setpoints for Fast Mineral Oil Analysis Using a Low Thermal Mass Oven

Injection	1 μL, splitless (0.4 min purge delay), 350 °C
Inlet liner	Split/splitless, p/n 5183-4647 (bottom taper, glass wool near top, 4 mm id)
SSI Inlet He pressure Program	[emulates constant flow mode] 120 kPa (0.5 min) to 160 kPa @ 40 kPa/min to 180 kPa (0.5 min) @ 20 kPa/min
Standard oven program	40 °C (0.5 min) to 340 °C (0.5 min) @ 15 °C/min [total run time = 21 min]
GC oven temp when using LTM	340 °C isothermal
LTM column program	40 °C (0.5 min), 200 °C/min to 240 °C, 100 °C/min to 340 °C (0.5 min) [total time = 3 min]
FID	340 °C, H ₂ = 40 mL/min, Air = 400 mL/min, N ₂ = 20 mL/min

Results and Discussion

System suitability was checked using a C₁₀-C₄₀ alkane test mixture. The obtained chromatogram is shown in Figure 1. Decane elutes at 0.8 min and is well separated from the solvent. Tetracosane elutes at 2.6 min. Retention time repeatability and peak area repeatability were determined for six runs and the results are summarized in Table 2.

The repeatability of retention times was excellent, with a standard deviation < 0.003 min (< 0.1% RSD). This effectively demonstrates that the LTM system reproducibly heats the capillary column. Peak area repeatability was also excellent (<1% RSD). This is due to the combination of fast autoinjection with an Agilent 7683B or 7693A ALS and appropriate liner selection.

Discrimination was checked against requirements by measuring the peak area ratio of C₄₀/C₂₀. In addition, discrimination for C₁₀/C₂₀ and C₄₀/C₁₀ were also determined and are presented in Table 2. The C₄₀/C₂₀ ratio was 0.899 (± 0.024), well above the method criterion (> 0.80). This provides a nice margin for maintaining compliance and demonstrates that the standard SSI inlet can meet method requirements. Splitless injection is also the most robust injection method and it is applicable to extracts from both “clean” samples such as surface water, and contaminated samples, such as soil or sediment.

Table 2. Figures of Merit

Solutes/sample	t _R (min) mean (n=6)	t _R s (min)	t _R (RSD%)	Peak Area mean (n=6)	Peak Area RSD (%)
C ₁₀	0.812	0.001	(0.06%)	4265000	0.86
C ₂₀	1.501	< 0.001	(< 0.01%)	4579000	1.05
C ₄₀	2.633	0.003	(0.10%)	4117000	0.85
Ratio C ₄₀ /C ₂₀ (*)				0.899	1.31
Ratio C ₁₀ /C ₂₀				0.935	0.97
Ratio C ₄₀ /C ₁₀				0.965	0.96
Mineral oil (**)	1.711	0.001	(0.03%)	408200000	0.64
RIVM C ₁₀ -C ₂₀				82490000	0.45
RIVM C ₂₀ -C ₄₀				111900000	0.24
RIVM ratio (***)				1.356	0.31

(*) ratio of C₄₀/C₂₀ should be > 0.80

(**) Restek cat. no. 31630, at 400 mg/L

(***) ratio of area sums C₂₀-C₄₀/C₁₀-C₄₀ should be between 1.25 and 1.40

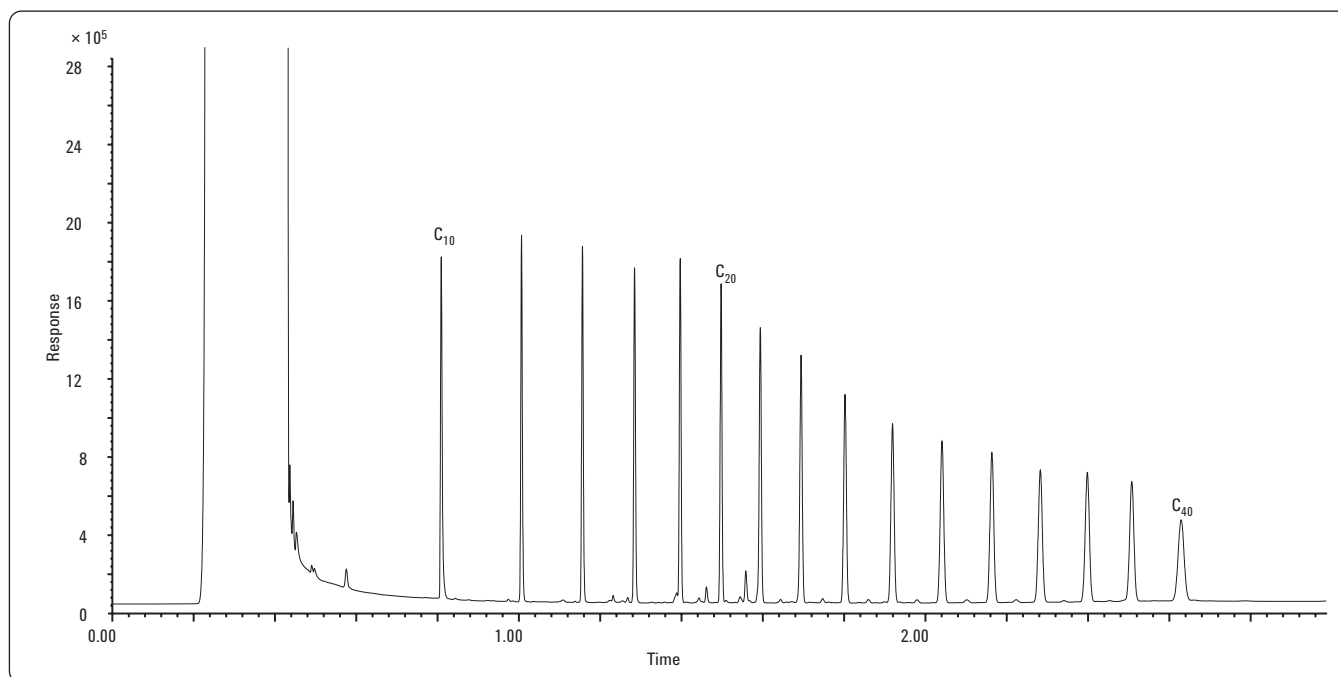


Figure 1. n-Alkane test mixture run with fast oven program on LTM oven module.

Next, a calibration mixture of diesel and motor oil was analyzed. The chromatogram for a 400 mg/L calibration sample is shown in Figure 2. The two “humps” corresponding to diesel and motor oil fractions can easily be detected. Calibration is normally done with a synthetic mineral oil made from a composite of diesel and motor oil in the concentration range from 100 to 1000 mg/L. The linearity of the fast GC-FID LTM method was tested from 40 mg/L to 1000 mg/L. The obtained calibration curve of the peak area (sum of peak area from end of decane peak to start of tetracosane peak) as a function of concentration is shown in Figure 3. The linearity was excellent ($r^2 > 0.999$). The repeatability of the peak area (sum C_{10} - C_{40}) of the calibration mixture at 400 mg/L was better than 1% RSD and the limit of detection was below 25 mg/L. As an additional benefit of fast oven programming, the hydrocarbon fraction is “compressed” into a narrower and higher “hump”. Therefore, method sensitivity is higher than standard methods that use slower temperature programming. A comparison of a standard oven program with the fast LTM

program (3-min run time) is shown in Figure 4 for a 400 mg/L sample. The “compression” and higher signal gained from the seven times faster LTM run is illustrated.

Additional discrimination testing was done using a popular reference sample from RIVM. Peak areas were measured for the C_{10} - C_{20} and C_{20} - C_{40} fractions. The mean peak areas ($n=6$) and corresponding RSDs are included in Table 2. The repeatability of peak area was again excellent with a relative standard deviation $< 1\%$. The ratio of the peak areas of the C_{20} - C_{40} fraction (“motor oil”) versus the C_{10} - C_{20} fraction (“diesel”) was 1.36 (0.31% RSD). These results are well within the specifications, since methods require a value to be between 1.25 and 1.40. This test also clearly shows that solute discrimination was minimal using a split/splitless inlet and fast autoinjection, and that the fast temperature program easily meets method performance criteria.

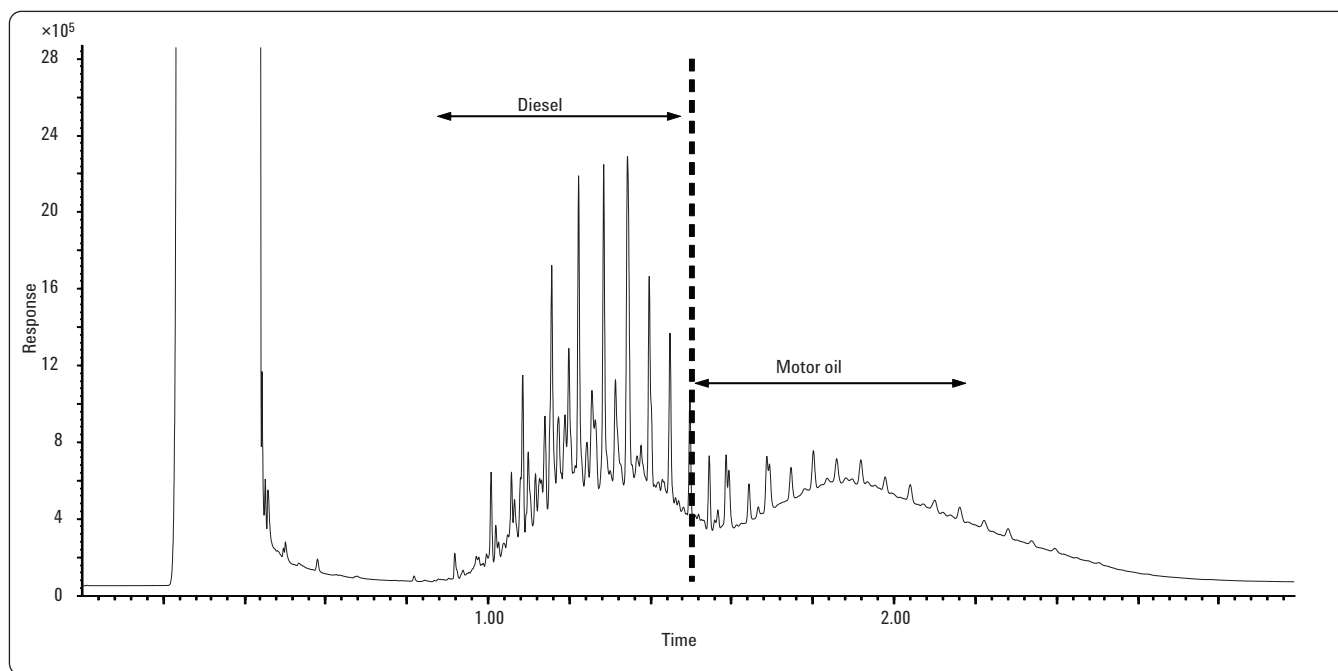


Figure 2. 400 mg/L calibration sample of diesel plus motor oil.

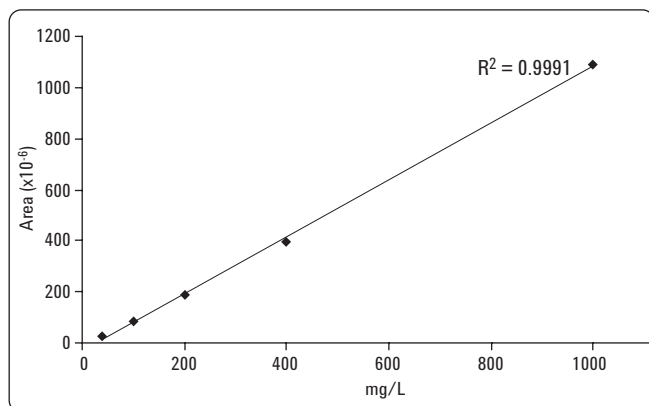


Figure 3. Mineral oil calibration. Calibration from 40 – 1000 mg/L. Linearity: $r^2 > 0.999$; repeatability at 400 mg/L: RSD on peak area = 0.64%; LOD: < 25 mg/L.

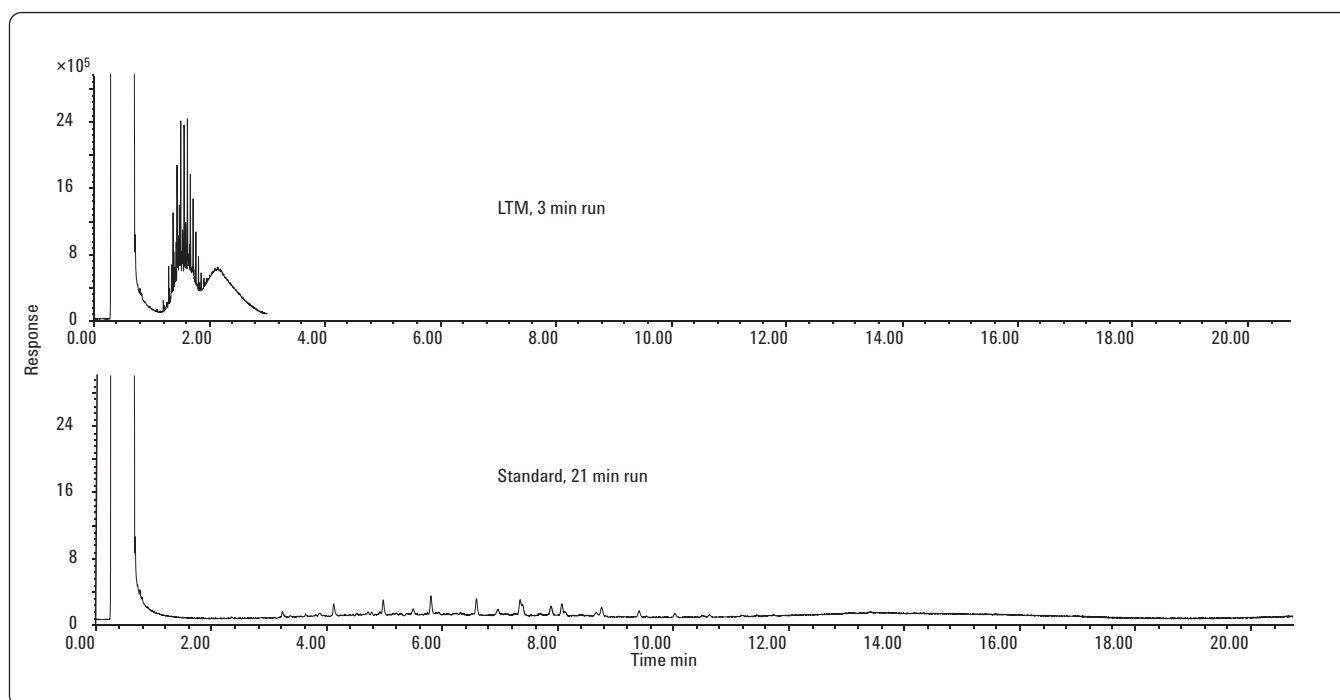


Figure 4. Comparison of sensitivity gain from fast LTM program to standard oven program. Diesel plus motor oil standard at 400 mg/L.

As can be deduced from the repeatability data, automatic integration of areas using fixed integration event times will remain valid and accurate for the whole C_{10} - C_{40} range, as well as for specific regions. These include smaller fractions such as C_{10} - C_{20} , C_{20} - C_{30} , and so forth, and reduces or eliminates the need for manual integration.

Conclusion

Great improvements can be achieved in the GC-FID analysis of mineral oil in environmental samples by adding an LTM module to an Agilent 7890A GC. Analysis time for the separation of C_{10} to C_{40} alkanes is below 3 min, and cool-down time to 40 °C was also very short (2 min). This results in a total injection-injection cycle time of 5 min. Excellent repeatability (retention times and peak areas), linearity and low LOD were achieved. The fast autoinjection allowed method criteria to be met using a standard hot SSI inlet.

References

1. International standard ISO 9377-2, Water Quality, Determination of hydrocarbon oil index, part 2: Method using solvent extraction and gas chromatography, 2000.
2. B. Wuest, Agilent Technologies application note 5988-0621EN, 2000.

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